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(54) PRODUCING P-TYPE CONDUCTIVITY IN SELF-COMPENSATING SEMICONDUCTOR MATERIAL

(54) METHODE DE PRODUCTION DE MATERIAUX SEMICONDUCTEURS DE TYPE P A AUTO-COMPENSATION

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ABSTRACT:

Abstract of the Disclosure
P-type self-compensated semiconductor materials and a process for producing them are described. The process includes imparting a region of P-type conductivity to the body of a self-compensated compound semiconductor material by the steps of preparing a crystal body of normally N-type self-compensated compound semiconductor material and bombarding said crystal body with charged particles such as beryllium ions.

CLAIMS: Show all claims

*** Note: Data on abstracts and claims is shown in the official language in which it was submitted.

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PRODUCING P-TYPE CONDUCTIVITY IN SELF-COMPENSATING SEMICONDUCTOR MATERIAL

Background of the Invention

Semiconductor materials of the compound type involving atoms from two different groups of the periodic table have been found to have many useful device properties. Many of these compound semiconductor materials have acquired the name intermetallics. Devices have been developed using compound type semiconductors where a particular property of the material is employed. However, in applying semiconductor device technology to compound semiconductor devices it is necessary to impart acceptor or p-type and donor or n-type conductivity to particular regions. There has heretofore been a number of the compound semiconductors that, while they had useful properties for devices, would exhibit only n-type conductivity. In these materials the conductivity effect of acceptor impurities is overcome or compensated by the spontaneous generation of lattice defects which have donor type ionization levels. In the common case these lattice defects are vacancies. This phenomenon is known in the art as vacancy self-compensation.

Description of the Invention

The invention involves introducing active, acceptor or p-type, conductivity sites into the crystal lattice by irradiation with electrons, protons or ions or by a combination of the introduction of p-type impurities followed by electron, proton or ion bombardment. The resulting capability

to produce p-type conductivity in compound semiconductor material enables one skilled in the art to employ the valuable properties of these materials which previously could only be obtained with n-type or insulating properties to make a wide variety of structures, heretofore unattainable. For example, there are a number of compound semiconductor materials that exhibit n-type conductivity only, that have energy gap widths that would permit electrical to light energy conversion at frequency and colors not readily achieved in semiconductor devices. In accordance with the teaching of this invention the full range of semiconductor structures will now be possible with these materials.

DESCRIPTION OF THE DRAWING

FIG. 1 is an energy diagram of a compound semiconductor material that exhibits self-compensation.

FIG. 2 is a flow chart illustrating steps employed to impart p-type conductivity in accordance with the invention.

FIG. 2A is a more detailed flow chart illustrating steps employed to impart p-type conductivity with resistivity control in accordance with the invention.

FIG. 2B is a still more detailed flow chart illustrating the interrelationship between ion implantation and charged particle irradiation.

FIG. 3 is a view of a two terminal semiconductor body having p-n junction therein.

DETAILED DESCRIPTION OF THE INVENTION

The class of materials to which this invention applies are those that could not be obtained with p-type conductivity heretofore because of the phenomenon of self-compensation. The phenomenon will occur when:

Equation 1: $E_c - E_v \geq \Delta H_f(V_B^x) + \Delta H_I(V_B^+)$

where $E_c - E_v$ is the fundamental bandgap of the semiconductor material; $\Delta H_f\ (V_B^x)$ is the enthalpy of formation of the neutral anion vacancy; and $\Delta H_I\ (V_B^+)$ is the ionization enthalpy of the anion vacancy to its donor state.

Referring to FIG. 1 an energy diagram is provided to assist in illustrating the phenomenon of self-compensation in compound semiconductors. The phenomenon occurs where the material generates enough lattice defects, commonly vacancies to compensate any concentration of impurities of the desired conductivity type. In practice the phenomenon has been observed to prevent p-type conductivity in large bandgap semiconductors where anion vacancies are more numerous than cation vacancies. The diagram shows the energy relationship of the maxima and minima of the valence and conduction bands, respectively, and the position of the fermi level. If the fermi level in this type of material were located near the valence band with a significant energy separation from a higher level which is the donor ionization level, then the total energy of the material could be lowered by generating an anion vacancy, ionizing same to its donor state, and allowing the resulting electron to drop to the fermi level. This process would cause the fermi level to rise away from the valence band, quenching p-type conductivity.

The energy separation between the donor energy level and the conduction band has been denoted in Equation 1 as $\Delta H_I(V_B^+)$ and refers to the ionization reaction.

Equation 2: $V_B^{x} \rightarrow V_B^{+} + e_c^{-}$

where V_B^{x} and V_B^{+} are the neutral and ionized donor states, respectively, of an anion vacancy V_B and e_c^{-} is an electron in the distribution of states at the bottom of the conduction band.

Once the reaction of Equation 2 takes place the electron e_c^{-} may fall to the fermi level releasing an energy $E_c - E_f$. Where E_c and E_f are as defined in FIG. 1.

Assuming $\Delta H_f(V_B^{x})$ is the energy required to produce a new anion vacancy, then if

Equation 3: $E_c - E_f > \Delta H_f(V_B^{x}) + \Delta H_I(V_B^{+})$

it will be apparent that it will be energetically favorable to create more anion vacancies, ionize them and drop the resulting electron to the fermi level.

As this occurs the fermi level will rise until

Equation 4: $E_c - E_f \leq \Delta H_f(V_B^{x}) + \Delta H_I(V_B^{+})$

at which condition self-compensation has taken place in the material preventing p-type conductivity.

The phenomenon of self compensation has been observed thus far in the art in at least the following compounds: gallium nitride (GaN); aluminum nitride (AlN); zinc oxide (ZnO); zinc sulfide (ZnS); cadmium sulfide (CdS) and cadmium selenide(CdS).

In accordance with the invention it is possible to impart p-type conductivity to normally self-compensating compound semiconductors that satisfy the conditions of Equation 1 by preparing a crystal of the material in accordance with the desired dopants and then irradiating the crystal with charged particles, for example, with electrons, protons or ions. This may be contrasted with the normal ion implantation used to

convert conductivity type wherein the concentration of implanted impurities overwhelms the concentration of existing impurities. Such overwhelming is accompanied by a large amount of crystal damage which must be anealed out to reveal the effect of the doping level. The ion implantation technique produces wide junctions. In other words the invention rearranges the crystal atoms to produce conductivity whereas ion implantation relies on implanted atoms to control conductivity.

In the fabrication of semiconductor devices it is necessary to have resistivity control. This control is provided by the differences between FIGS. 2 and 2A.

Referring to FIGS. 2 and 2A flow charts are provided to illustrate the operations required in imparting p-type to a normally n-type compound semiconductor. The first operation is to prepare the normally n-type compound semiconductor crystal for charged particle irradiation. The preparation operation involves insuring that the crystal surface through which the irradiation is to take place is free of material that would inhibit or disturb evenness under the appropriate conditions for that operation. In instances where it is desirable to impart added flexibility in resistivity control the preparation may include an added step of introduction of an acceptor impurity and may also be accompanied by inhibiting loss of donors through a coating.

Referring to FIG. 2 the flow chart sets forth a crystal preparation step, which in the broadest case consists of crystal surface condition control capable of permitting uniform, even, charged particle irradiation for example, by proton (H^+) bombardment. The irradiation step consists of placing the crystal in a vacuum chamber under conditions such that a charged particle is supplied with sufficient electric field stress to insure penetration of the crystal to the desired depth and concentration. The necessary electric field stress is influenced by the mass

of the particle. In order to provide more dopant flexibility acceptor impurities can be first introduced prior to irradiation.

Referring to FIG. 2A the preparation step is expanded to include the use of a coating. The coating reduces loss of anion atoms during processing. When this coating is made of an acceptor and a charged particle irradiation is made therethrough, the acceptor concentrations can be enhanced in the step. Where appropriate the coating may also be used for contact metallurgy purposes in the final device.

Referring next to FIG. 2B the crystal is prepared for uniform introduction of dopants and charged particles through a surface thereof. Acceptors are then introduced into the crystal by the technique of ion implantation which may be followed by an annealing step. The crystal is then coated to reduce nitrogen vacancy loss in subsequent processing. The crystal is lastly irradiated with charged particles to convert to p-type.

In order to enable one skilled in the art to more easily comprehend the invention the following is an explanation as the state of the art has developed thus far, of the physics resulting from the steps and the structure, as applied to a particular material, aluminum nitride (AlN) using a particular charged particle, the proton (H^+) for irradiation. It should be understood by one skilled in the art that the knowledge of physical mechanisms within compound semiconductor crystals is constantly evolving so that a particular physical mechanism should not be viewed as essential to the practice of the invention.

The light particle or proton bombardment is believed to create a situation where an atom of the crystal lattice is placed in an interstitial position leaving a vacancy in its substitutional site. This situation is known in the art as a Frenkel pair and is represented for the material AlN as

Equation 5: $Al_{Al} \longrightarrow Al_i + V_{Al}$

and

Equation 6: $N_N \longrightarrow N_i + V_N$

where Al_i and N_i refer to interstitial atoms, V_{Al} and V_N are neutral aluminum and nitrogen vacancies respectively and the subscripts Al and N denote the aluminum and nitrogen lattice sites respectively.

The interstitial atoms thus created migrate randomly through the crystal and would be expected to occupy the first vacant lattice site encountered. One can adjust the bombardment step so that the number of Al and N vacancies created will be essentially equal. When the number of bombarding protons (H^+) is sufficient to create a number of Al vacancies and of N vacancies equal to the number of N vacancies initially present, the redistribution of interstitial atoms will override the vacancy self-compensation conditions in the crystal as set forth in equations 1 to 4 and a net p-type conductivity will result. The reaction is illustrated in the following relationship:

Equation 7: $$V_N^+ + e^- \xrightarrow{\text{BOMBARDMENT}} 2V_N^+ + V_{Al}^- + N_i + Al_i + e^- \xrightarrow[\text{MIGRATION}]{\text{INTERSTITIAL}}$$

$$\tfrac{2}{3}Al_N^{-2} + \tfrac{1}{3}Al_{Al} + \tfrac{1}{3}N_{Al}^{+2} + \tfrac{2}{3}N_N + \tfrac{2}{3}V_N^+ + \tfrac{1}{3}V_{Al}^- + \tfrac{1}{3}e^+$$

where e^- is an electron and e^+ is a hole. V_N+ is the ionized nitrogen vacancy. V_{Al}^- is the ionized aluminum vacancy Al_N^{-2} is an doubly ionized aluminum atom on a nitrogen site. N_{Al}^{-2} is a doubly ionized nitrogen atom on an aluminum site.

Where the concentration of N vacancies in the vacancy self-compensated compound semiconductor material before processing is less than that of other donor and deeply trapping impurities and defects already in the material or where lower resistivity values are desired, the vacancy

concentration can be increased as set forth in connection with FIG. 2A where acceptor impurities in addition to those already present are added to the material before bombardment. The acceptor impurities can be incorporated during crystal growth, introduced by diffusion or added by the ion implantation technique well known in the art. Considerable flexibility is available with these techniques on depth and concentration.

The addition of acceptor impurities to the example material AlN would increase the concentration of N vacancies. Prior to the conversion step in Equation 7 the acceptor impurity level in the material would be compensated but would be relatively shallow. The addition of acceptor impurities will not only increase the concentration of nitrogen vacancies but will enhance the p-type conductivity after the bombardment step.

An acceptor impurity for addition should be selected on the basis of some of the following attributes. It should have a high solubility in the material of the host crystal. It should act as a single acceptor if located on an acceptor lattice site. It should act as a triple acceptor if located on a donor lattice site. It should have a sufficiently low mass that in reaction with the host crystal a low bombardment threshold energy is required. Lastly, as an interstitial, it should diffuse rapidly and not have the tendency to form interstitial complexes. For the example material AlN, the acceptor impurity beryllium is particularly attractive. The reaction in addition to Equation 7 for the ideal case would be as follows:

Equation 8: $$V_N^{+} + Be^{-}_{Al} \xrightarrow{\text{BOMBARDMENT}} Be_i + V_{Al}^{-} + V_N^{+} \xrightarrow[\text{MIGRATION}]{\text{INTERSTITIAL}} V_{Al}^{-} + Be_N^{-3} + 4e^{+}$$

Referring next to FIG. 3 a p-n junction device fabricated in accordance with the invention is illustrated. The device is made up of a

supporting substrate of an electrically and thermally conductive material such as copper to which an electrical lead 2 can be applied. The self-compensated compound semiconductor material member 3 is made up of an n-type conductivity region 4 and joined at a P-N junction 5 with a p-type conductivity region 6 to which is attached an electrical lead 7. Where the member 3 is made of AlN, the n-type conductivity region 4 is formed by the technique well known in the art of chemical vapor deposition wherein an AlN layer is deposited using a sintered AlN source. The region 4 is of low resistance n-type conductivity. A region 6 of beryllium (Be) doped AlN is sputtered on the region 4 until a depth of about 2000 angstroms is achieved.

The region 6 is then vacuum coated with a layer of beryllium (Be) 400 to 700 angstroms thick. The region 6 is then implanted with beryllium (Be) ions at a fluence of approximately 10^{15} ions per square centimeter at a voltage of 140 kilovolts. This produces a p-type layer 6 of approximately 2000 angstroms thick with a "hole" concentration of 10^{19} per CC, a mobility of about 1000 cm^2 $volt^{-1}$ sec^{-1} and a resistivity of about 10^{-3} ohms cm.

The beryllium, in addition to its being an acceptor dopant produces cation Frenkel pairs in a quantity great enough to convert the material.

It should be noted that the beryllium (Be) serves the role of a source of acceptors, the protective coating to prevent the out diffusion of nitrogen atoms, the charged particles in irradiation and the external electrical connection. Electrical connections 2 and 7 are made to region 1 and the beryllium coating respectively. The resulting device when appropriately connected electrically performs such two terminal semiconductor device functions, such as assymetric conductivity and electrical energy to light conversion.

While a two terminal semiconductor p-n junction device has been shown it will be readily apparent to one skilled in the art that the teaching of imparting p-type conductivity of this invention is readily extendable to the range of semiconductor technology.